

P/ INT COOPERATION TREA

PCT

NOTIFICATION OF ELECTION

(PCT Rule 61.2)

From the INTERNATIONAL BUREAU

To:

Assistant Commissioner for Patents
 United States Patent and Trademark
 Office
 Box PCT
 Washington, D.C.20231
 ETATS-UNIS D'AMERIQUE

in its capacity as elected Office

Date of mailing (day/month/year) 15 August 2000 (15.08.00)	
International application No. PCT/NL00/00018	Applicant's or agent's file reference P21918PC00
international filing date (day/month/year) 13 January 2000 (13.01.00)	Priority date (day/month/year) 15 January 1999 (15.01.99)
Applicant BUWALDA, Pieter, Lykle et al	

1. The designated Office is hereby notified of its election made:



in the demand filed with the International Preliminary Examining Authority on:

11 July 2000 (11.07.00)



in a notice effecting later election filed with the International Bureau on:

2. The election ☒ was

was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland Facsimile No.: (41-22) 740.14.35	Authorized officer Pascal Piriou Telephone No.: (41-22) 338.83.38
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PATENT COOPERATION TREATY

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference P21918PC00	FOR FURTHER ACTION		see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.
International application No. PCT/NL 00/ 00018	International filing date (day/month/year) 13/01/2000	(Earliest) Priority Date (day/month/year) 15/01/1999	

Applicant

COÖPERATIEVE VERKOOP- EN PRODUCTIEVERENIGING ...

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 2 sheets.

☒ It is also accompanied by a copy of each prior art document cited in this report.

1. Basis of the report

a. With regard to the language, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

☐ the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

b. With regard to any nucleotide and/or amino acid sequence disclosed in the international application, the international search was carried out on the basis of the sequence listing:

☐ contained in the international application in written form.

☐ filed together with the international application in computer readable form.

☐ furnished subsequently to this Authority in written form.

☐ furnished subsequently to this Authority in computer readable form.

☐ the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

☐ the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

2. ☐ Certain claims were found unsearchable (See Box I).

3. ☐ Unity of invention is lacking (see Box II).

4. With regard to the title,

☐ the text is approved as submitted by the applicant.

☒ the text has been established by this Authority to read as follows:

HYDROPHOBIC STARCH DERIVATIVES

5. With regard to the abstract,

☒ the text is approved as submitted by the applicant.

☐ the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the drawings to be published with the abstract is Figure No.

☐ as suggested by the applicant.

☐ because the applicant failed to suggest a figure.

☐ because this figure better characterizes the invention.

☒ None of the figures.

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INTERNATIONAL SEARCH REPORT

International Application No.

PC 00/00018

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08B35/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 824 161 A (SÜDZUCKER AG) 18 February 1998 (1998-02-18) page 7, line 30-34; claims 1,5,6,15,46; example 3	1-5, 9, 11, 12
A	EP 0 799 837 A (COÖPERATIEVE VERKOOP- EN PRODUCTIEVERENIGING VAN AARDAPPELMEEL ...) 8 October 1997 (1997-10-08) page 3, line 9-48; claims 1-3,12; examples 1-5	1-12
A	EP 0 761 691 A (NATIONAL STARCH AND CHEMICAL INVESTMENT) 12 March 1997 (1997-03-12) page 4, line 3-8; claims 1,2,5; examples I, II	1-12

☐ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

15 March 2000

Date of mailing of the international search report

22/03/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Radke, M

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/JP 00/00018

Patent document cited in search report		Publication date		Patent family member(s)		Publication date
EP 0824161	A	18-02-1998	AT	403705 B		25-05-1998
			AT	404606 B		25-01-1999
			AT	144496 A		15-09-1997
			AT	27097 A		15-05-1998
EP 0799837	A	08-10-1997	NL	1002782 C		09-10-1997
EP 0761691	A	12-03-1997	US	5672699 A		30-09-1997
			AU	710985 B		07-10-1999
			AU	5223796 A		13-03-1997
			CA	2185035 A		07-03-1997
			JP	9110902 A		28-04-1997

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From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

PCT

NOTIFICATION OF TRANSMITTAL OF
THE INTERNATIONAL PRELIMINARY
EXAMINATION REPORT

(PCT Rule 71.1)

To:

Mr Ir A.W. Prins, C.S.
C/O VEREENIGDE

Nieuwe Parklaan 97
NL 2587 BN The Hague

PAYS-BAS
14 NOV. 2000

NRF₂ 15-7-2001

Com RB

Date of mailing
(day/month/year)

09.11.2000

Beantwoord
voorl.
def.

bericht gezonden
aan
dd.

MAP

Applicant's or agent's file reference
P21918PC00

St. 13 PP 1/2

IMPORTANT NOTIFICATION

International application No.
PCT/NL00/00018

International filing date (day/month/year)
13/01/2000

Priority date (day/month/year)
15/01/1999

Applicant

COÖPERATIEVE VERKOOP- EN PRODUCTIEVERENIGING ...

1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary examination report and its annexes, if any, established on the international application.
2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.
3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.

4. REMINDER

The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices) (Article 39(1)) (see also the reminder sent by the International Bureau with Form PCT/IB/301).

Where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary examination report. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.

For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide.

Name and mailing address of the IPEA/



European Patent Office
D-80298 Munich
Tel. +49 89 2399 - 0 Tx: 523656 epmu d
Fax: +49 89 2399 - 4465

Authorized officer

Aperribay, I

Tel. +49 89 2399-8154



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PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)


Applicant's or agent's file reference P21918PC00	FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/NL00/00018	International filing date (day/month/year) 13/01/2000	Priority date (day/month/year) 15/01/1999
International Patent Classification (IPC) or national classification and IPC C08B35/00		
Applicant COÖPERATIEVE VERKOOP- EN PRODUCTIEVERENIGING ...		

- This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.
- This REPORT consists of a total of 6 sheets, including this cover sheet.
 - ☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of 2 sheets.

3. This report contains indications relating to the following items:

- I ☒ Basis of the report
- II ☐ Priority
- III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☒ Certain defects in the international application
- VIII ☒ Certain observations on the international application

Date of submission of the demand 11/07/2000	Date of completion of this report 09.11.2000
Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized officer Radke, M Telephone No. +49 89 2399 8677 <div data-bbox="1404 1837 1559 1974" data-label="Image"> </div>

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INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/NL00/00018

I. Basis of the report

1. This report has been drawn on the basis of (*substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments.*):

Description, pages:

1-25 as originally filed

Claims, No.:

1-12 as received on 27/09/2000 with letter of 27/09/2000

2. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
☐ the claims, Nos.:
☐ the drawings, sheets:

3. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

4. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	1-12
	No:	Claims	
Inventive step (IS)	Yes:	Claims	1-12
	No:	Claims	
Industrial applicability (IA)	Yes:	Claims	1-12
	No:	Claims	

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**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/NL00/00018

2. Citations and explanations

see separate sheet

VII. Certain defects in the international application

The following defects in the form or contents of the international application have been noted:

see separate sheet

VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

see separate sheet

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Re Item V

Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Cited literature

(a) The following documents (D) are referred to in this report:

D1EP-A-0 824 161

D2EP-A-0 799 837

D3EP-A-0 761 691.

(b) In the following arguments, page or column A, lines B to C will be cited as A/B-C.

2. Novelty

(a) Document **D1** is considered to represent the closest prior art for the assessment of novelty. **D1** describes in example 3 (see 12/21) the reaction product of **amylopectin potato starch** with **butylene** oxide (DS 0,025) and 2,3-epoxypropyl trimethylammonium chloride (DS 0,04).

The preferred amylose content is from 0 to 3 % (see 7/30-34).

(b) The subject-matter of **claims 1 to 12** is novel since **D1** does not teach to treat the amylopectin starch with a hydrophobic agent comprising an alkyl chain having **seven** to 24 carbon atoms.

3. Inventive step

(a) The subject-matter of **claims 1 to 12** is also deemed to be inventive.

(b) The problem to be solved in the present application was to provide a hydrophobic starch which shows associative behaviour, which may be formed into a reversible gel and which has excellent rheology regulating properties, such as high viscosity

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when dissolved or dispersed in water (see 2/12-18 of the present description).

Document **D1** is not the proper starting point for the present invention since it deals with a completely different problem, i.e. to reduce the absorption of liquids by paper (see **D1**, 3/5-24).

(c) Document **D2** describes an aqueous composition comprising

- (a) amylopectin potato starch and
- (b) an emulsifier

in the form of a viscous liquid or a gel (see claims 1-3).

Example 4 shows that waxy maize starch will yield less viscosity and gelling effect than amylopectin potato starch (see 6/41-46). Further advantages of amylopectin potato starch are mentioned at 3/9-15. The amylopectin potato starch may be chemically modified (3/45-48).

Document **D2** may be considered to represent the closest prior art for the assessment of inventive step since it addresses gel formation and viscosity increase, i.e. aspects of the present problem.

- (d) Document **D3** describes in the examples the reaction of waxy maize starch with alkenylsuccinic acid anhydrides (alkenyl = dodecenyl, octenyl, C₁₆+C₁₈-alkenyl).
- (e) It was, however, not obvious to combine the teachings of **D3** and **D2** in order to solve the present problem since **D3** deals with a totally different problem, i.e. to impart hydrophobicity to paper (see **D3**, 4/3-8).
- (f) For this reason, the subject-matter of **claims 1 to 12** is based on an inventive step.

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**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/NL00/00018

Re Item VII

Certain defects in the international application

Contrary to the requirements of Rule 5.1(a)(ii) PCT, the relevant background art disclosed in the document **D1** is not mentioned in the description, nor is this document identified therein.

Re Item VIII

Certain observations on the international application

1. The following features found in the claims have been omitted from the description. Therefore, the description does not provide support for the claims as required by Article 6 PCT. The features in question are:
 - (a) The additional feature of **claim 2**.
 - (b) In **claim 5**: "carboxylic acid".
 - (c) The additional features of **claims 6 and 7**.
2. The description is not adapted to the amended claims.

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27. 09. 2000

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(59)

Amended Claims

1. A process for preparing a hydrophobic starch, comprising etherification, esterification or amidation of a root or tuber starch comprising at least 95 wt.% of amylopectin, based on dry substance of the starch, or a derivative thereof, with a hydrophobic reagent comprising an alkyl chain
5 having from 7-24 carbon atoms.
2. A process according to claim 1, wherein the starch comprises at least 98 wt.% of amylopectin, based on dry substance of starch.
3. A process according to any of the preceding claims, wherein the starch is amylopectin potato starch or amylopectin tapioca starch.
- 10 4. A process according to any of the preceding claims, wherein the derivative of the starch is obtained by hydroxyalkylation, carboxymethylation, cationization, partially degradation, oxidation, or a combination thereof.
5. A process according to any of the preceding claims, comprising etherification using a hydrophobic reagent comprising a halide, halohydrin,
15 epoxide, glycidyl, carboxylic acid or quaternary ammonium group.
6. A process according to any of the preceding claims, comprising esterification using a hydrophobic reagent comprising an anhydride group.
7. A process according to any of the preceding claims, comprising amidation of a carboxymethylated starch using a hydrophobic reagent
20 comprising an amine group.
8. A process according to any of the preceding claims, wherein the etherification, esterification or amidation is carried out in the presence of a surfactant.
9. A hydrophobic starch obtainable in a process according to any of the
25 preceding claims.

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10. A reversible gel comprising a hydrophobic starch according to claim 9 dispersed in water.
11. The use of a hydrophobic starch according to claim 9 as a rheology regulating agent.
- 5 12. The use according to claim 11, wherein the rheological regulating agent is used in the food, textile or paper industries, in personal care products, bioplastics, water-based coatings, adhesives or inks.

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AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
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BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
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CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
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DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

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INTERNATIONAL SEARCH REPORT

Int. Application No

PCT/NL 00/00018

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08B35/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 824 161 A (SÜDZUCKER AG) 18 February 1998 (1998-02-18) page 7, line 30-34; claims 1,5,6,15,46; example 3	1-5, 9, 11, 12
A	EP 0 799 837 A (COÖPERATIEVE VERKOOP- EN PRODUCTIEVERENIGING VAN AARDAPPELMEEL ...) 8 October 1997 (1997-10-08) page 3, line 9-48; claims 1-3,12; examples 1-5	1-12
A	EP 0 761 691 A (NATIONAL STARCH AND CHEMICAL INVESTMENT) 12 March 1997 (1997-03-12) page 4, line 3-8; claims 1,2,5; examples I, II	1-12

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

15 March 2000

Date of mailing of the international search report

22/03/2000

Name and mailing address of the ISA

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INTERNATIONAL SEARCH REPORT

information on patent family members

Inte Application No

PCT/NL 00/00018

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0824161 A	18-02-1998	AT 403705 B	25-05-1998
		AT 404606 B	25-01-1999
		AT 144496 A	15-09-1997
		AT 27097 A	15-05-1998
EP 0799837 A	08-10-1997	NL 1002782 C	09-10-1997
EP 0761691 A	12-03-1997	US 5672699 A	30-09-1997
		AU 710985 B	07-10-1999
		AU 5223796 A	13-03-1997
		CA 2185035 A	07-03-1997
		JP 9110902 A	28-04-1997

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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁷ : C08B 35/00		A1	(11) International Publication Number: WO 00/42076
			(43) International Publication Date: 20 July 2000 (20.07.00)
(21) International Application Number: PCT/NL00/00018		(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).	
(22) International Filing Date: 13 January 2000 (13.01.00)			
(30) Priority Data: 99200111.5 15 January 1999 (15.01.99) EP			
(71) Applicant (for all designated States except US): COÖPERATIEVE VERKOOP- EN PRODUCTIEVERENIGING VAN ARDAPPELMEEL EN DERIVATEN AVEBE B.A. [NL/NL]; Beneden Oosterdiep 27, NL-9641 JA Veendam (NL).			
(72) Inventors; and		Published	
(75) Inventors/Applicants (for US only): BUWALDA, Pieter, Lykle [NL/NL]; Mondriaanstraat 32, NL-9718 MJ Groningen (NL). KESSELMANS, Ronald, Pieter, Wilhelmus [NL/NL]; Kromkampen 11, NL-9468 HK Annen (NL). MAAS, Augustinus, Arnoldus, Maria [NL/NL]; De Ree 7, NL-9753 BX Haren (NL). SIMONIDES, Hylke, Hotze [NL/NL]; Rozemarijnstraat 29, NL-9731 HJ Groningen (NL).		With international search report.	
(74) Agent: OTTEVANGERS, S., U.; Vereenigde, Nieuwe Parklaan 97, NL-2587 BN The Hague (NL).			
(54) Title: HYDROPHOBIC STARCH DERIVATIVES			
(57) Abstract			
<p>The invention relates to a process for preparing a hydrophobic starch, comprising etherification, esterification or amidation of a root or tuber starch comprising at least 95 wt.% of amylopectin, based on dry substance of the starch, or a derivative thereof, with a substituent comprising an alkyl chain having from 4-24 carbon atoms. The invention further relates to a hydrophobic starch obtainable by said process.</p>			

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BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

Title: HYDROPHOBIC STARCH DERIVATIVES

The invention relates to a process for preparing a derivative of starch of a hydrophobic nature, as well as to a derivative obtainable in said process.

Hydrophobically modified biopolymers, such as
5 polysaccharides, find application in, *inter alia*, the textile and paper industries, in personal care products, bioplastics, water-based coatings, adhesives and inks. When dissolved or dispersed in water, these compounds possess favorable foaming and surface tension properties. Further, such compounds
10 provide enhanced viscosification of aqueous solutions or dispersions containing the compounds.

It is believed that viscosity enhancement from increased hydrophobe content of such solutions or dispersions may be due to intermolecular association of individual
15 polysaccharide molecules through the presence of hydrophobic groups or molecules to form polymeric networks. Support for this association has been observed in the rheology of the solutions. At relatively low shear rates up to 12 reciprocal secs, the solutions exhibit only mild pseudoplasticity at
20 higher viscosities and near Newtonian behavior at lower viscosities. However, at shear rates of 200 reciprocal secs, the viscosity drops to very low values. This non-linear shear thinning behavior is consistent with the formation of intermolecular bridges by the presence of hydrophobic groups
25 or molecules. Introduction of charged groups, which has conventionally been used for viscosity enhancement, has a number of disadvantages, such as sensitivity to the presence of salts. For instance, increased cationic substitution by quaternary nitrogen substituents which do not contain
30 hydrophobic groups or molecules, causes a reduction in the solution viscosity at a constant high shear. It is believed that the increased cationic repulsion between molecules inhibits the formation of hydrophobe bridging resulting in a breakdown in the polymer network in solution.

Hydrophobically modified polymers, where the backbone is a cellulosic polymer, have been shown to possess an associative behavior. However, no associative behavior has been observed when the backbone is formed by starch.

5 Järnström et al., in Nordic Pulp and Paper, Research journal, no. 3/1995, pp. 183-189, have described five different modified starches, of which three were hydrophobically modified by reaction with octenyl substituted succinic anhydride. They have observed that in relative concentrated
10 solutions of these three hydrophobic starches, no associative behavior occurs.

The present invention aims to provide a hydrophobic starch which does show associative behavior. It is further an object of the invention to provide a hydrophobic starch which
15 may be formed into a reversible gel. Yet another object of the invention is to provide a hydrophobic starch having excellent rheology regulating properties, such as a high viscosity when dissolved or dispersed in water.

It has been found that the above goals can be
20 achieved by using a specific type of starch as the basis for the hydrophobic starch. Thus, the invention relates to a process for preparing a hydrophobic starch, comprising etherification, esterification or amidation of a root or tuber starch comprising at least 95 wt.% of amylopectin,
25 based on dry substance of the starch, or a derivative thereof, with a substituent comprising an alkyl chain having from 4-24 carbon atoms.

A process according to the invention leads in a highly convenient manner to the objective hydrophobic starch.
30 The hydrophobic starch obtainable by said process has been found to show associative behavior. This associative behavior leads to a viscosity enhancement of the hydrophobic starch in solution, and may even lead to the formation of gels. As opposed to viscosity enhancement due to the introduction of
35 charged groups, viscosity enhancement resulting from hydrophobic interaction shows a slight increase in the

presence of salts. Further, the hydrophobically modified starch has an increased surface activity in comparison with non-modified starch.

Without wishing to be bound by theory, it is believed
5 that associative behavior of the present hydrophobically modified starch in aqueous solutions occurs through interaction of the hydrophobic alkyl groups attached to the starch molecules. Hydrophobic groups often tend to cluster into aggregates, such as micelles or vesicles. The driving
10 force for this cluster formation is believed to arise from the tendency of the hydrophobic groups to minimize the disruption of the water structure around the starch. Associating between hydrophobic alkyl groups may occur between alkyl chains having a certain minimum chain length.
15 If the alkyl chain is too short, the chains attached to the polymer molecules cannot come close enough to each other to interact. Furthermore, the degree of substitution of the alkyl groups has to exceed a certain critical limit to give noticeable interaction.

20 The product obtainable by said process has excellent properties, making it an extremely suitable rheology regulating agent. It has been observed, for instance, that when a solution of a hydrophobic starch according to the invention having a viscosity of 200 mPa.s is added to a
25 solution of native starch or starch derivative, also having a viscosity of approximately 200 mPa.s, an enormous increase in viscosity takes place. Also, the present hydrophobic starch is highly suitable to be used as an emulsifying agent, and as such has a stabilizing effect on an emulsion. In addition,
30 the product may be formulated into a reversible gel. Furthermore, the hydrophobic starch provides a better spread on low energy surfaces. As a result, the hydrophobic starch has very good adhesion properties on these low energy surfaces.

35 As has been indicated above, in a process according to the invention, a starch is used, which starch has a very

high amylopectin content. Most starch types consist of granules in which two types of glucose polymers are present. These are amylose (15-35 wt.% on dry substance) and amylopectin (65-85 wt.% on dry substance). Amylose consists of unbranched or slightly branched molecules having an average degree of polymerization of 1000 to 5000, depending on the starch type. Amylopectin consists of very large, highly branched molecules having an average degree of polymerization of 1,000,000 or more. The commercially most important starch types (maize starch, potato starch, wheat starch and tapioca starch) contain 15 to 30 wt.% amylose.

Of some cereal types, such as barley, maize, millet, wheat, milo, rice and sorghum, there are varieties of which the starch granules nearly completely consist of amylopectin. Calculated as weight percent on dry substance, these starch granules contain more than 95%, and usually more than 98% amylopectin. The amylose content of these cereal starch granules is thus less than 5%, and usually less than 2%. The above cereal varieties are also referred to as waxy cereal grains, and the amylopectin starch granules isolated therefrom as waxy cereal starches.

In contrast to the situation of different cereals, root and tuber varieties of which the starch granules nearly exclusively consist of amylopectin are not known in nature. For instance, potato starch granules isolated from potato tubers usually contain about 20% amylose and 80% amylopectin (wt.% on dry substance). During the past 10 years, however, successful efforts have been made to cultivate by genetic modification potato plants which, in the potato tubers, form starch granules consisting for more than 95 wt.% (on dry substance) of amylopectin. It has even been found feasible to produce potato tubers comprising substantially only amylopectin.

In the formation of starch granules, different enzymes are catalytically active. Of these enzymes, the granule-bound starch synthase (GBSS) is involved in the

formation of amylose. The presence of the GBSS enzyme depends on the activity of genes encoding for said GBSS enzyme.

Elimination or inhibition of the expression of these specific genes results in the production of the GBSS enzyme being

5 prevented or limited. The elimination of these genes can be realized by genetic modification of potato plant material or by recessive mutation. An example thereof is the amylose-free

mutant of the potato (amf) of which the starch substantially only contains amylopectin through a recessive mutation in the

10 GBSS gene. This mutation technique is described in, inter

alia, J.H.M. Hovenkamp-Hermelink et al., "Isolation of

amylose-free starch mutant of the potato (*Solanum tuberosum*

L.)", Theor. Appl. Genet., (1987), 75:217-221, and E. Jacobsen

et al., "Introduction of an amylose-free (amf) mutant into

15 breeding of cultivated potato, *Solanum tuberosum* L.,

Euphytica, (1991), 53:247-253.

Elimination or inhibition of the expression of the GBSS gene in the potato is also possible by using so-called

antisense inhibition. This genetic modification of the potato

20 is described in R.G.F. Visser et al., "Inhibition of the

expression of the gene for granule-bound starch synthase in

potato by antisense constructs", Mol. Gen. Genet., (1991),

225:289-296.

By using genetic modification, it has been found

25 possible to cultivate and breed roots and tubers, for

instance potato, yam, or cassave (Patent South Africa

97/4383), of which the starch granules contain little or no

amylose. As referred to herein, amylopectin potato starch is

the potato starch granules isolated from potato tubers and

30 having an amylopectin content of at least 95 wt.% based on

dry substance.

Regarding production possibilities and properties,

there are significant differences between amylopectin potato

starch on the one hand, and the waxy cereal starches on the

35 other hand. This particularly applies to waxy maize starch,

which is commercially by far the most important waxy cereal

starch. The cultivation of waxy maize, suitable for the production of waxy maize starch is not commercially feasible in countries having a cold or temperate climate, such as The Netherlands, Belgium, England, Germany, Poland, Sweden and Denmark. The climate in these countries, however, is suitable for the cultivation of potatoes. Tapioca starch, obtained from cassave, may be produced in countries having a warm climate, such as is found in regions of South East Asia and South America.

The composition and properties of root and tuber starch, such as amylopectin potato starch and amylopectin tapioca starch, differ from those of the waxy cereal starches. Amylopectin potato starch has a much lower content of lipids and proteins than the waxy cereal starches.

Problems regarding odor and foaming, which, because of the lipids and/or proteins, may occur when using waxy cereal starch products (native and modified), do not occur, or occur to a much lesser degree when using corresponding amylopectin potato starch products.

According to the present invention, the amylopectin starch to be used is a root or tuber starch. It has been found that the presence of the lipids and proteins adversely affects the hydrophobation reaction, leading to by-products because of which the hydrophobic starch is not of sufficient quality. Moreover, hydrophobic starch based on an amylopectin root or tuber starch has been found to show highly favorable hydrophobic behavior.

The use of amylopectin potato starch and amylopectin tapioca starch has been found to lead to particularly advantageous hydrophobic starches.

In a preferred embodiment, a derivative of a starch type as described above is used. Especially, derivatives obtainable by hydroxyethylation, hydroxypropylation, carboxymethylation, cationization, degradation, hydrolysis (possibly enzymatic), oxidation or a combination thereof, are useful. The use of a suitable derivative leads to a

hydrophobic starch having an improved reactivity, stability, solubility, complexation, enzyme resistance and/or other properties. Particularly, hydroxypropylation has been found to have a beneficial effect on the stability of the resulting hydrophobic starch. It is also possible to perform the hydrophobation first, and then prepare a suitable derivative by hydroxyethylation, hydroxypropylation, carboxymethylation, cationization, degradation and/or oxidation to improve the stability, solubility, complexation, enzyme resistance, and other properties of a product obtainable by a process according to the invention. The amount of additional substitution, i.e. molar substitution defined as the average moles of such substituent per mole of glucose units, designated MS, is not critical but may be any amount desired, depending on the envisaged application of the product.

The molecular weight of the starch used for preparing a hydrophobic starch according to the invention is an important factor in controlling the viscosity and rheological properties of the hydrophobic starch to be prepared.

Preferably, the molecular weight of the starch is decreased before, during or after the hydrophobation reaction. A decrease in molecular weight may be accomplished by oxidation or degradation, e.g. by a reaction of the starch with sodium hypochlorite, hydrogen peroxide, ozone, an acid, or the like. In a preferred embodiment, the starch is first degraded or oxidized and then a hydrophobic group is introduced. It is within the skill of the artisan to determine the extent of oxidation or degradation desirable for a certain envisaged application of the hydrophobic starch.

In a process according to the invention, a hydrophobic substituent is attached to the specific starch described above by an ether, ester or amide group. When the hydrophobic group is attached to the starch via an ether linkage, the hydrophobic reagent preferably comprises a halide, halohydrin, epoxide or glycidyl group as reactive site. The alkyl chain of the agent can vary from 4-24 carbon

atoms, preferably from 7-20 carbon atoms. Suitable examples of hydrophobic reagents to provide an ether linkage are cetyl bromide, lauryl bromide, butylene oxide, epoxidized soybean fatty alcohols, epoxydized linseed fatty alcohols, allyl glycidyl ether, propyl glycidyl ether, butyl glycidyl ether, decane glycidyl ether, lauryl glycidyl ether, lauryl phenyl glycidyl ether, myristoyl glycidyl ether, cetyl glycidyl ether, palmityl glycidyl ether, stearyl glycidyl ether, linolyl glycidyl ether and mixtures thereof. Other etherification agents which may be used to react with starch in accordance with the invention are alkyl halides containing at least four carbon atoms, such as 1-bromodecane, 10-bromo-1-decanol, and 1-bromododecane.

In a preferred embodiment a charged hydrophobic group is introduced. A hydrophobic cationic group can be attached via an ether linkage by reaction of the starch with a reagent comprising a quaternary ammonium group, for example a 1-chloro-2-hydroxypropyltrialkyl ammonium salt or a glycidyltrialkyl ammonium salt. The alkyl chains of this quaternary ammonium group can vary from 1-24 carbon atoms, preferably from 7-20 carbon atoms, wherein at least one of the alkyl chains of the quaternary ammonium group comprises 4-24 carbon atoms. Preferably, the other alkyl chains have less than 7 carbon atoms. For example 1-chloro-2-hydroxypropyldimethyl-lauryl ammonium salt, 1-chloro-2-hydroxypropyldimethylmyristoyl ammonium salt, 1-chloro-2-hydroxypropyldimethylcetyl, 1-chloro-2-hydroxypropyldimethylstearyl, glycidyldimethyl-lauryl ammonium salt, glycidyldimethylmyristoyl ammonium salt, glycidyldimethylcetyl ammonium salt, glycidyldimethylstearyl ammonium salt, dialkylaminoethyl halide, or mixtures of the above can be applied as hydrophobic cationization reagent. A hydrophobic cationic group may be introduced by reaction with tertiary ammonium groups such as chloroethyldialkylamine hydrogen chloride salt. The alkyl chain of this tertiary ammonium group may vary from 1 to 24 carbon atoms. The reaction for

introducing the hydrophobic cationic group may be performed analogous to the procedure disclosed in EP-A-0 189 935. A hydrophobic anionic group can be attached applying a 2-chloro-aminodialkyl acid as reagent, for instance analogous to the procedure disclosed in EP-A-0 689 829.

When the hydrophobic group is attached to the starch via an ester linkage, several kinds of reagents, such as alkyl anhydrides can be applied. The alkyl chain can vary from 4-24 carbons, preferably from 7-20 carbons. Especially, mixed anhydrides as octanoic acetic anhydride, decanoic acetic anhydride, lauroyl acetic anhydride, myristoyl acetic anhydride are suitable alkyl anhydrides.

In a preferred embodiment, hydrophobic anionic groups may be attached to the amylopectin starch. This may be accomplished by reaction of the specific starch with an alkyl succinic anhydride or alkenyl succinic anhydride. The alkyl chain can vary from 4-24 carbons, preferably from 7-20 carbons. Octenyl succinic anhydride, nonyl succinic anhydride, decyl succinic anhydride, dodecenyl succinic anhydride are most commonly applied. The procedure in accordance with this embodiment may be performed analogous to the procedures disclosed in US-A-5,776,476.

For the preparation of a hydrophobic group linked to carboxymethyl amylopectin starch by an amide group the procedure as described in WO-A-94/24169 can analogously be applied. Examples of suitable reagents for introduction of an amide group include fatty amines comprising saturated or unsaturated hydrocarbon groups having from 8 to 30 carbon atoms. Branched hydrocarbon groups are not excluded, but linear chains are preferred. Preferably, the fatty radical originates from a C_{12} to C_{24} fatty amine. Particularly favorable results are obtained if the fatty amine is selected from the group consisting of n-dodecylamine, n-hexadecylamine, n-octadecylamine, cocoamine, tallowamine, hydrogenated N-tallow-1,3-diaminopropane, N-hydrogenated tallow-1,3-diaminopropane, and N-oleyl-1,3-diaminopropane.

Such fatty amines are known under the trade names Armeen and Duomeen (AKZO Chemicals).

The degree of hydrophobic substitution, i.e. DS, defined as the average number of moles of hydrophobic substituents per mole glucose units, achieved in a process according to the invention, may vary depending upon the presence of other substituents in the starch prior to the hydrophobation, the type of hydrophobic reagent used, and the envisage application of the product. Generally, the DS will be greater than zero, preferably from 0.0001 to about 0.4, more preferably from 0.001 to 0.2, and most preferably from 0.002 to 0.1. It is surprising to note that even a very small DS leads to a relatively large effect.

The hydrophobation of amylopectin root or tuber starch may be performed under semi-dry reaction conditions, in suspension (water or organic solvent), in aqueous solution (dispersion), or during the gelatinization of the amylopectin potato starch granules. It is also possible to perform the hydrophobation in an extruder at increased temperature and pressure. According to the latter embodiment, it is possible to perform the reaction continuously. The moisture content is preferably smaller than 25% when the reaction is carried out in an extruder.

Preferably, water is used as a solvent when the reaction is performed in suspension. When the hydrophobic reagent has a low solubility in water, combinations of water and suitable water mixable organic solvents may be employed. Suitable organic solvents include, but are not limited to, methanol, ethanol, i-propanol, n-propanol, t-butanol, sec-butanol, methylethylketon, tetrahydrofuran, dioxan, and acetone.

The reaction in aqueous solution is preferably performed using a reaction mixture comprising more than 20 wt.% of the starch or derivative thereof and less than 80 wt.% of the solvent. More preferably, the starch content in the reaction mixture lies between 20 and 40 wt.%, whereas the

solvent content preferably lies between 80 and 60 wt.%. An autoclave in combination with a dryer (drum dryer; spray dryer) or an extruder is preferably used as a reaction vessel. The reaction is further performed under conditions which are well-known for analogous reactions. The pH lies preferably between 7 and 13.

Preferably, a process according to the invention is performed in the presence of a caustic catalyst, such as an alkali metal hydroxide or the like material. In accordance with specific embodiments, the caustic catalyst is used in such amounts that it is in fact present as a reagent.

Further, it has been found that the reaction for preparing a hydrophobic starch according to the invention can be accelerated by the presence of one or more surfactants in the reaction mixture. Suitable surfactants are characterized by the ability to facilitate bringing the hydrophobic reagent in contact with the hydrophilic starch, so reaction can take place (phase-transfer catalysis). In accordance with this embodiment, the reaction is preferably performed while the reaction mixture is stirred. Surfactants can be applied in any of the above mentioned reaction systems. The surfactants which may be used include nonionics, anionics, cationics or amphoterics, singly or in combination provided they are compatible with the other components of the reaction system and they are capable to facilitate bringing the hydrophobic reagent in contact with the hydrophilic starch. Examples of suitable surfactants are higher fatty alcohol sulfates, such as a sodium or potassium sulfate of an alcohol having from 8 to 18 carbon atoms, alkylphenoxypolyethoxyethanols, such as octylphenoxypolyethoxyethanols, alkyltrimethylammonium halides and alkyltributylammonium hydroxides, such as tetramethylammonium hydroxide and cetyltrimethylammonium bromide, alkyl acids, such as stearic acid, an ethylene oxide condensate of a long-chain alcohol, such as lauryl, or cetyl alcohol, polyoxyethylene sorbitan' stearate, and many others. Preferably, the surfactant comprises a branched alkyl chain

or multiple alkyl chains. The amounts wherein the surfactants are used may vary between 0.1 and 10 wt.%, based on dry substance of starch.

5 As has been mentioned above, it is one of the great advantages of the invention, that a product obtainable by a process as disclosed herein above, may be used to form a reversible gel.

10 A hydrophobic starch obtainable in a process as disclosed above may be used in the paper industry, for instance in surface sizing or coatings, or in the textile industry, for instance as textile warp size. In addition, the present product may find application in personal care products, for instance for the retention of oils, perfumes, emollients and the like; in hair and skin care compositions
15 including water-in-oil or oil-in-water emulsions, lotions, detergents, creams, soaps, cleansers, sunscreens, shampoos, rinses, conditioners, antidandruff aids. Further, the product may be applied as carrier for active agents in, for example, internal drugs (controlled release), in dispersants, as flow
20 control aids in flocculants, as thickeners, in antistatic softeners, or as topically active agents to various substrates such as metal, glass and so on. The product may further be used in various food products, such as noodles, emulsifying agents, e.g. beverage emulsifiers, low fat
25 products, spreads, sauces, dressings, batters, and dry seasoning mixes. Other applications include the use of the product in bioplastics, water-based coatings, adhesives and inks, such as employed in ink-jet recording sheets.

30 The invention will now be elucidated by the following non-restrictive examples.

EXAMPLES**Methods****Determination of the degree of substitution of an alkylsuccinic ester by saponification**

The degree of substitution (DS) is defined as the amount of ester in mole per mole of glucose units. The degree of substitution of alkylsuccinic esters is measured according to the following procedure.

- Approximately 10 g (dry substance) product and 10 mL methanol are mixed. The mixture is poured into 50 mL water. The suspension is stirred and some drops of a phenolphthalein solution in 50 weight % ethanol are added. The suspension is titrated with a 0.1 N aqueous NaOH solution to light red. Then 25.00 mL of 0.1 N aqueous NaOH solution is added. The mixture is stirred at 40 °C during 24 hours and then the mixture is cooled to room temperature and titrated to colorless with 0.1 N aqueous HCl solution. Beside, the ester substituted products also a non-substituted product is measured as control. The DS is calculated with the formula:

$$DS = (162 + 0.1x(25.00 - A)) / (B - (Y + 0.1x(25.00 - A))),$$

wherein

A = mL 0.1 N HCl of the product - mL 0.1 N HCl of the control

B = mg product (dry substance)

Y = 210 if substituent is octenylsuccinic ester

Y = 266 if substituent is dodecenylsuccinic ester or tetrapropenylsuccinic anhydride

Brabender viscosity

- To characterize starch and starch derivatives, a Brabender viscograph is generally used to record a viscosity curve, the viscosity is expressed in Brabender units (BU).

In this case the heating and cooling step is 1.5 °C per minute, rotation 75 rpm, torque 250 cmg and the concentration 3%.

5 The suspension is heated from room temperature to 90°C and kept at that temperature for 20 min. Thereafter, the dispersion is cooled to 30 °C.

In the tables shown below, the viscosity after 20 minute at 90° (BU₉₀₋₂₀) and the viscosity after cooling to 30 °C are given.

10

Brookfield viscosity

A suspension of 2 weight % of starch in demineralized water is heated at 90 °C under stirring for 20 minutes. The
15 resulting dispersion is cooled to 20 °C and the Brookfield viscosity is measured with a Brookfield RVF viscometer (20 rpm; spindle 4).

After the determination of the viscosity the starch dispersion was sheared for 1 minute with an Ultra-Turrax T50
20 at 10.000 rpm. After 2 hours the Brookfield viscosity after shear was measured at 20°C.

Example 1

25 The preparation of an octenylsuccinic ester of starch

A suspension of 5 mole starch in water (39 % dry matter) was prepared. The suspension was stirred at 25 °C and the pH was adjusted to 8.5 by the addition of an aqueous 4.4 wt. % NaOH solution. To the suspension the octenylsuccinic
30 anhydride was added slowly in an amount sufficient to obtain the desired DS. During addition the pH of the reaction mixture was kept constant at 8.5.

After 4 hours reaction the reaction mixture was neutralized to pH 5.0. Subsequently, the crude product was
35 filtered over a Büchner funnel, washed with 5 L water, and suspended in 2 L methanol. This suspension was stirred for 1

hour at room temperature and the product again was filtered over a Büchner funnel. The starch ester was washed with 5 L water and dried at room temperature.

5 The type of starch (potato starch, amylopectin potato starch or waxy maize starch) and the degree of substitution was varied (D_{smax} 0.02, 0.03 or 0.04). The Brabender viscosities of the products were measures. The results are shown in Table 1.

10 Example 2

The preparation of a dodecenylsuccinic ester or tetrapropenylsuccinic ester of starch

15 A suspension of 5 mole starch in water (39 % dry matter) was prepared. The suspension was stirred at 25 °C and the pH was adjusted to 8.5 by the addition of an aqueous 4.4 w/w% NaOH solution. To the suspension the alkylsuccinic anhydride was added slowly in an amount to obtain the desired DS. During addition the pH of the reaction mixture was kept constant at 8.5. After 23 hours reaction the reaction mixture
20 was neutralized to pH 5.0. Subsequently, the crude product was filtered over a Büchner funnel, washed with 5 L water, and suspended in 2 L methanol. This suspension was stirred for 1 hour at room temperature and the product again was filtered over a Büchner funnel. The starch ester was washed
25 with 5 L water and dried at room temperature.

The type of starch (potato starch, amylopectin potato starch or waxy maize starch), the reagent (dodecenylsuccinic anhydride or tetrapropenylsuccinic anhydride, 0.05 mole). The Brabender viscosities of the resulting products are shown in
30 Table 1.

Table 1 - Brabender viscosity of the different alkylsuccinic esters of different starch types

Type of starch	Alkylsuccinic ester	DS (mole/mole)	Brabender viscosity (BU)	
			at 20 °C	at 30 °C
Potato	Octenylsuccinic	0.015	960	1690
	Dodecenylsuccinic	0.008	860	1550
Amylopectin potato	none	none	700	960
	Octenylsuccinic	0.013	2040	2370
		0.019	2380	2830
		0.023	2580	3000
	Dodecenylsuccinic	0.005	1400	3220
	Tetrapropenylsuccinic	0.016	2090	2720
Waxy maize	Octenylsuccinic	0.017	1320	1520
	Dodecenylsuccinic	0.005	290	560
	Tetrapropenylsuccinic	0.016	1210	1660

5

Example 3

The preparation of amylopectin potato starch has increased Brabender viscosity in a lauryl cationic starch ether

10 A suspension of 2.5 mole starch in water (39 % dry matter) was prepared. The suspension was stirred at 35 °C. To the suspension the X mole 1-chloro-2-hydroxypropyl-dimethyl lauryl ammonium chloride was added. Subsequently, (X + 0.125) mole NaOH was added as an aqueous 4.4 w/w% NaOH solution over a period of 1 h.

15 After 24 hours reaction the reaction mixture was neutralized to pH 5.0 with hydrochloric acid, washed with 2.5 L water and dried at room temperature.

20 The type of starch (potato starch, amylopectin potato starch or waxy maize starch) and the degree of substitution (DS) was varied. The Brookfield viscosity of the products were measured as indicated above. The results are summarized in Table 2.

As can be seen in the table the Brookfield viscosity of solutions of the hydrophobic amylopectin starch before and

after high shear is much higher in comparison to the viscosity of the derivatives based on potato and waxy maize starch. Note the hydrophobic amylopectin potato starch derivatives are less sensitive towards the high shear treatment.

Table 2 - Brookfield viscosity (before and after high shear) of the lauryl cationic ethers of different types of starch

Type of starch	DS (mole/mole)	Brookfield viscosity (mPa.s.)	
		before shear	after shear
Potato	0.04	5650	745
Amylopectin potato	0.04	14800	2080
	0.06	14400	3290
Waxy Maize	0.06	4200	255

Example 4

The preparation of a hydroxyalkyl ether of starch

A mixture of 2.5 mole starch and 5 g NaOH was suspended in 500 mL isopropyl alcohol. To the suspension was added 500 mL of demineralized water and the reaction mixture was heated to 70 °C. To the mixture 250 mmol glycidyllauryl ether was added.

After 4 days stirring the reaction mixture was cooled to room temperature, neutralized with 6 N HCl, filtered over a Büchner funnel, washed successively with 2.5 L water and 0.5 L ethanol, and dried at room temperature.

During reaction some samples were taken to determine the epoxide content. This content was measured according to the next procedure.

The total weight of the reaction suspension was measured. A sample of 5.00 g of the suspension was taken. This sample is filtered over a G4 filter and washed successively with 50 mL of water and 50 mL of ethanol. The filtrate was brought in an Erlenmeyer. The temperature of the solution was raised to 75 °C and a few drops of an aqueous

Thymol Bleu solution (0.04 weight %) was added. The mixture was titrated with HCl till the color turned yellow and then 25.0 mL of a sodium thiosulfate solution in water (30 weight %) was added. After 30 minutes the raised pH was titrated with 0.1 N HCl solution until the bleu solution colored yellow. The epoxide content and the yield of the reaction were calculated according to the formulas:

• Epoxide content (mmol) = (mL 0.1 N HCl) x 0.1 x A
wherein A = (Total weight of the suspension)/5.00

• Yield (%) = (Epoxide content)/250 x 100%

Table 3 - Yield

Reaction after .. days	Yield
0	87 %
2	47 %
4	23 %

Example 5

The preparation of a hydroxyalkyl ether of hydroxypropyl starch

To an alkaline solution (pH > 12) of 7.5 mole of hydroxypropylated amylopectin potato starch (DS_{max} = 3.0) in 1.7 L water stirred at 80 °C were added 375 mmoles of glycidyl lauryl ether. The reaction was stirred for another 4.5 h at 80 °C and allowed to come to room temperature.

During the reaction, some samples were taken to determine the epoxide content as discussed in example 4. Of the reaction mixture, 20 g was dissolved in 80 mL water and 50 mL ethanol was added. The mixture was heated to 75 °C. The epoxide content and the yield of the reaction was determined according to the procedure described in example 4.

Table 4 - Yield

Reaction after .. hours	Yield
½	87 %
2	68 %
4½	46 %

Example 65 Adhesive performance

The adhesive performance of hydrophobized amylopectin potato starch was determined in comparison to non-hydrophobized amylopectin potato starch. As test material octenylsuccinic ester of hypochlorite oxidized amylopectin potato starch was used. These octenylsuccinic ester (DS_{max} 0.02) was prepared from hypochlorite oxidized amylopectine potato starch according to the procedure described in example 1.

• Preparation of an adhesive composition

15 The octenylsuccinic esters of amylopectin potato starch was intensively mixed with demineralized water at room temperature. The pulverized starch derivative was poured in the water under continuously stirring, the applied mass ratio starch : water = 1 :4, respectively, yielding a solution with a solid content of approximately 20%. The prepared adhesive was evaluated for practical adhesion when applied between a paper substrate and a polyethylene coated (hydrophobic) paper substrate.

• Adherents

25 Kraft; 85 g/m². Cut into a strip with dimensions: 250 x 30 mm.

30 PE coated Kraft; 90 g/m². A PE layer of 20 g/m² on top of a Kraft layer of 70 g./m². The surface tension of the PE surface is adjusted to approximately 40 mN/m by a Corona treatment (for a discussion of a Corona treatment, see e.g. D. Briggs and C.R. Kendall, "Chemical Basis of Adhesion to Electrical Discharge Treated Polyethylene", Polymer 20, 1053-1054, (1979), or R. Kruger and H. Potente, "Corona-

Discharge Treatment of Polypropylene Films - Effects of Process Parameters", J. Adhesion, 11, 113-124, (1980)). Cut into a strip with dimensions: 250 x 40 mm.

- Dry solids

5 The concentration of an adhesive composition is determined by means of a refractometer (Atago AX-1000; 20 °C), and presented as a brix value.

- Viscosity

10 The viscosity of a adhesive composition is determined by means of a viscometer (Brookfield RVF; 20 rpm, reading after 5 turns).

- Practical adhesion

15 The practical adhesion is determined in a T-peel test, using a universal testing machine (Zwick 1446; load cell 100 N). The test is performed in a conditioning room capable of maintaining a relative humidity of $50\% \pm 2\%$ at $23 \pm 1^\circ\text{C}$. The adherents are stored under the same conditions. A adhesive composition is tested 16-24 hours from the moment of preparation. A thin film (60 μm) of an adhesive composition
20 is applied on the Kraft strip (sieve side) by means of a wire winded rot. Immediately the glued paper is placed on the PE coated side of the other adherent, and pressed between two plates and pressed with 5 kg for one minute. The remaining adhesive joint is clamped between specimen grips and pulled
25 apart at different time intervals: 5, 10, 15, 20, 25, 30, 45, 60 minutes. The test path has a length of 50 mm, the speed is set at 400 mm/min. The practical adhesion is represented by the force of resistance observed in the T-peel test. Fiber tear is clearly observed at a resistance force of 2500 mN/mm.
30 This level is used as an arbitrary value to discriminate between the setting time of different adhesive compositions.

- Performance

35 The performance of the adhesive composition in terms of viscosity and practical adhesion, are summarized in Table 5.

Table 5 - Viscosity and setting time of octenylsuccinic esters of hypochlorite oxidized amylopectin potato starch

DSmax	Concentration (Brix %)	Viscosity (mPa.s)	Setting time at 2500mN/mm (minute)
0.00	21.0	860	47
0.02	20.6	1100	23

5 From the results, it can be concluded that a decrease of the setting time and thus an improved adhesion is obtained when the amylopectin starch is hydrophobized.

10

Example 7

Emulsifying properties

Emulsions of the oil-in-water (O/W) type were prepared.

15 The products were prepared as described in example 1 and 3. These products were drumdried as suspension to make them cold-water soluble. Solutions of these products were prepared in demineralized water in a concentration of 2 weight %. To 180 g of a stirred solution 20 g of paraffin oil (Merck p.a.) was added. The stirring was continued for 1
20 minute and then the emulsion was homogenized for 2 minutes with an Ultra Turrax T25 high shear mixer. The emulsion was allowed to stand overnight at 40°C. The results are summarized in Table 6.

25

Table 6 - Emulsifying properties of hydrophobized starches.

Starch type	Substituent	DSmax	Emulsion Stability after 24 hours
Amylopectin potato	none	none	Free oil, unstable
	octenylsuccinic ester	0.03	Stable
	hydroxypropyldimethyl- ammoniumlauryl ether,	0.08	Stable
Potato	hydroxypropyldimethyl- ammoniumlauryl ether	0.08	Creaming, unstable

In the table can be seen that only hydrophobic amylopectin potato starch derivatives give stable emulsions.

5

Example 8

Thickening behavior of hydrophobic modified amylopectine potato starch as a result of the addition of sodium chloride

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The hydroxypropyltrimethylammonium ether (DS_{max} 0.125) of amylopectine potato starch is prepared in suspension with

3-chloro-2-hydroxypropyltrimethylammonium chloride as described in example 3. A 39 wt%. suspension was drum dried.

15

The combined hydroxypropyldimethylammoniumlauryl and hydroxypropyltrimethylammonium ether of amylopectine potato starch is prepared in an one-pot suspension reaction with 3-chloro-2-hydroxypropyldimethylammoniumlauryl chloride (DS_{max} 0.04) and 3-chloro-2-hydroxypropyltrimethylammonium chloride

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(DS_{max} 0.06) as described in example 3. A 39 wt%. suspension of the derivative was drum dried. The hydroxypropyl, hydroxypropyldimethylammoniumlauryl double ether is prepared by first a reaction of amylopectin potato starch in suspension with 3-chloro-2-hydroxypropyldimethyl-

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ammoniumlauryl chloride (DS_{max} 0.08) as described in example 3. Subsequently, a reaction in solution in an autoclave with propylene oxide (DS_{max} 0.5) was carried out to hydroxypropylate the derivative according to known procedures. The product was drum drying.

30

Solutions of these products were prepared in demineralized water in a concentration of 10 weight %. To these solutions sodium chloride was added in different concentrations. After addition of salt the solutions were stirred for 30 minutes before the Brookfield viscosity was

35

measured. The results are summarized in Table 7.

Table 7 - Viscosity of hydrophobized amylopectin potato starch in the presence of sodium chloride

Substituent	DS _{max}	NaCl (weight %)	Viscosity (mPa.s)
none	none	0.0	2120
		1.0	2000
		5.0	2025
		10	2100
hydroxypropyltrimethylammonium ether	0.125	0.0	1100
		5.0	975
		10	1025
hydroxypropyldimethylammoniumlauryl ether and hydroxypropyltrimethylammonium ether	0.04 and 0.06	0.0	16800
		1.0	28000
		5.0	30000
		10	53000
hydroxypropyldimethylammoniumlauryl ether and hydroxypropyl ether	0.08 and 0.5	0.0	47000
		1.0	122600
		5.0	100600
		10	84000

From the results, it can be concluded that the hydrophobic amylopectin potato starch shows an increase of the viscosity due to the addition of sodium chloride. Thus, the hydrophobic starch shows associate behavior.

Example 9

Noodle seasoning paste

Noodle seasoning paste samples with were prepared according to the recipe as shown in table 8. The octenylsuccinic esters of potato and amylopectin potato starch with both a DS_{max} of 0.03 were prepared according to the procedure as described in example 1.

As can be seen in Table 8, the hydrophobic interaction of the octenylsuccinic ester of amylopectin potato starch is higher than the interaction of the same derivative of potato starch. This results in a much lower dosage of the amylopectin potato starch derivative in the recipe.

Table 8 - Stability of recipes of noodle seasoning paste.

	control	octenylsuccinic ester of potato starch	octenylsuccinic ester of amylopectin potato starch
Recipe (weight %)			
Starch	none	4.8 %	3.5 %
Water	9.2 %	8.7 %	8.8 %
Dark soy sauce	9.2 %	8.7 %	8.8 %
Spices	31.2 %	29.8 %	30.2 %
Oil	50.4 %	48.9 %	48.7 %
Paste stability	Oil separation	Stable	Stable

5

Example 10

Thickening of starch solutions with hydrophobic starch

10 A cationic amylopectin potato starch derivative (hydroxypropyltrimethylammonium chloride; DS = 0.027) was dissolved in demineralized water in 1.0 weight %. This solution was mixed with a 1.0 weight % solution of a lauryl cationic starch ether (DS = 0.088), prepared according to example 3.

15 The mixed solutions (1.0 weight %) were heated to 90 °C and cooled to room temperature. The Brookfield viscosities are summarized in Table 9.

20 Table 9 - Brookfield viscosities (spindle Helipath) of mixtures of hydrophobic starch and cationic starch.

Fraction of lauryl cationic starch (%)	Fraction of cationic starch (%)	Brookfield viscosity (mPa.s.)
0.0	100.0	< 100
25.0	75.0	10600
50.0	50.0	10400
75.0	25.0	4000
100.0	0.0	200

As can be seen in Table 9, a remarkable increase of the viscosity is found when a solution of starch (derivative) is mixed with a solution of a hydrophobized amylopectin potato starch.

Claims

1. A process for preparing a hydrophobic starch, comprising etherification, esterification or amidation of a root or tuber starch comprising at least 95 wt.% of amylopectin, based on dry substance of the starch, or a derivative thereof, with a hydrophobic reagent comprising an alkyl chain having from 4-24 carbon atoms.
2. A process according to claim 1, wherein the starch comprises at least 98 wt.% of amylopectin, based on dry substance of starch.
3. A process according to any of the preceding claims, wherein the starch is amylopectin potato starch or amylopectin tapioca starch.
4. A process according to any of the preceding claims, wherein the derivative of the starch is obtained by hydroxyalkylation, carboxymethylation, cationization, partially degradedation, oxidation, or a combination thereof.
5. A process according to any of the preceding claims, comprising etherification using a hydrophobic reagent comprising a halide, halohydrin, epoxide, glycidyl, carboxylic acid or quaternary ammonium group.
6. A process according to any of the preceding claims, comprising esterification using a hydrophobic reagent comprising an anhydride group.
7. A process according to any of the preceding claims, comprising amidation of a carboxymethylated starch using a hydrophobic reagent comprising an amine group.
8. A process according to any of the preceding claims, wherein the etherification, esterification or amidation is carried out in the presence of a surfactant.
9. A hydrophobic starch obtainable in a process according to any of the preceding claims.
10. A reversible gel comprising a hydrophobic starch according to claim 9 dispersed in water.

11. The use of a hydrophobic starch according to claim 9 as a rheology regulating agent.

12. The use according to claim 11, wherein the rheological regulating agent is used in the food, textile or paper industries, in personal care products, bioplastics, water-based coatings, adhesives or inks.

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INTERNATIONAL SEARCH REPORT

 Int. Application No
 PCT/NL 00/00018

 A. CLASSIFICATION OF SUBJECT MATTER
 IPC 7 C08B35/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

 Minimum documentation searched (classification system followed by classification symbols)
 IPC 7 C08B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 824 161 A (SÜDZUCKER AG) 18 February 1998 (1998-02-18) page 7, line 30-34; claims 1,5,6,15,46; example 3	1-5,9, 11,12
A	EP 0 799 837 A (COÖPERATIEVE VERKOOP- EN PRODUCTIEVERENIGING VAN AARDAPPELMEEL ...) 8 October 1997 (1997-10-08) page 3, line 9-48; claims 1-3,12; examples 1-5	1-12
A	EP 0 761 691 A (NATIONAL STARCH AND CHEMICAL INVESTMENT) 12 March 1997 (1997-03-12) page 4, line 3-8; claims 1,2,5; examples I,II	1-12

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

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